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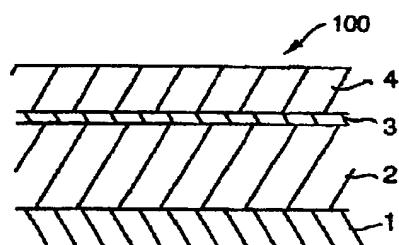
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(54) Exhaust gas purifying catalyst

(57) An exhaust gas purifying catalyst includes at least an under catalytic layer disposed on a substrate containing a NOx absorbent which absorbs NOx in exhaust gas under existence of oxygen, releases absorbed NOx when an oxygen concentration of exhaust gas lowers and is restrained from absorbing NOx by sulfur compounds in exhaust gas and an outer oxide layer disposed over the under catalytic layer and containing a Ce-Zr composite oxide.

FIG. 1



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Description

5 The present invention relates to an exhaust gas purifying catalyst for a lean burn gasoline engine and a diesel engine.

10 It has been known to install a NO_x absorbent in an exhaust passage, the NO_x absorbent absorbs NO_x in the exhaust gas while an air-fuel mixture has an air-to-fuel ratio on a lean side and releases the NO_x for deoxidization and purification when the oxygen concentration of the exhaust gas is lowered. Typically this type of NO_x absorbent has the property of easily absorbing SO_x (sulfur compounds: sulfuric acid ions and sulfurous acid ions are included) rather than NO_x in the exhaust gas. In consequence, the NO_x absorbent that has been poisoned by SO_x (which is hereafter referred to SO_x-poisoning) encounters a significant reduction in NO_x adsorption performance. With respect to sulfur compounds poisoning of the NO_x absorbent, Japanese Unexamined Patent Publication No. 8 - 192051 describes an exhaust gas purifying catalyst that comprises a carrier comprising a composite oxide of Ti and Zr, and a catalytic noble metal and a NO_x absorbent which are carried by the composite oxide. This exhaust gas purifying catalyst employs Pt as the catalytic noble metal and at least one selected from a group including alkaline earth metals, alkali metals and rare earth elements as the NO_x absorbent. In the exhaust gas purifying catalyst, a Ti-Zr composite oxide easily absorbs SO_x, since the NO_x absorbent causes a reduction in the probability of contacting to SO_x, it is thought that the NO_x absorbent is prevented from SO_x poisoning. The Ti-Zr composite oxide has a high acidity, so that it is thought that it is advantageous to improving NO_x conversion efficiency of the exhaust gas purifying catalyst.

20 30 As a result of a study by the inventor of this application, it was revealed that though the Ti-Zr composite oxide absorbs NO_x and is, however, hard to absorb SO_x, it somewhat weakened its NO_x absorption property as well as its SO_x absorption property and, in consequence, the NO_x absorbent caused not only a reduction in the probability of contacting to SO_x but a significantly great reduction in the probability of contacting to NO_x, it is thought that the NO_x absorbent is prevented from SO_x poisoning. That is, even when NO_x in the exhaust gas approached the NO_x absorbent, the Ti-Zr composite oxide by which NO_x absorbent kept the NO_x off the NO_x absorbent, the NO_x was hardly absorbed by the NO_x absorbent.

35 40 It is therefore an object of the invention to provide an exhaust gas purifying catalyst which does not exhibit the disadvantages of known catalysts as mentioned above. The present invention provides an exhaust gas purifying catalyst which comprises not a catalytic layer whith a NO_x absorbent and a high acid material mixed therein but an under catalytic layer disposed on a substrate and containing a NO_x absorbent and an outer high acid layer.

45 50 The invention further provides an exhaust gas purifying catalyst comprising an under catalytic layer disposed on a substrate and containing a NO_x absorbent and a high acid outer oxide layer in which SO_x is prevented from reaching the NO_x absorbent in the under catalytic layer by the high acid outer layer and NO_x is absorbed by the NO_x absorbent without blocking by the high acid layer when NO_x reaches the under catalytic layer so as to cause SO_x escape easily from the under catalytic layer.

55 According to an aspect of the present invention, the exhaust gas purifying catalyst comprises a catalytic layer disposed on a substrate and containing a NO_x absorbent which absorbs NO_x in exhaust gas under existence of oxygen, releases the absorbed NO_x when an oxygen concentration of exhaust gas lowers and is restrained from absorbing NO_x by sulfur compounds

in exhaust gas, and an oxide layer disposed over the under catalytic layer and containing a Ce-Zr composite oxide.

The Ce-Zr composite oxide is one of oxides which have an ionic electric field strength of approximately $0.7 \text{ e}\cdot\text{\AA}^{-2}\text{\AA}$ (where $e = 1.6021892 \times 10^{-11} \text{ C}\cdot\text{m}^{-2}\text{\AA}$). Sulfur oxides (SO_x) in exhaust gas are, on the one hand, easily absorbed by compounds having high basicity and, on the other hand, hardly absorbed by oxides having high acidity. Therefore, sulfur oxides in exhaust gas are diffused only a little in quantity in the under catalytic layer due to blocking by the Ce-Zr composite oxide containing oxide layer, so as to prevent poisoning the NO_x absorbent in the under catalytic layer. In consequence, the sulfur concentration becomes lower in the under catalytic layer than in the outer oxide layer. While NO_x in exhaust gas diffuse in and penetrate through the outer oxide layer and are absorbed by the NO_x absorbent in the under catalytic layer, the Ce-Zr composite oxide in the oxide layer is considered to somewhat block diffusion and penetration of NO_x and, however, does not prevent the penetrated NO_x from being absorbed by the NO_x absorbent. Further, while the NO_x absorbent in the under catalytic layer is somewhat poisoned by sulfur oxides penetrating the outer oxide layer, since sulfur oxides which are released from the NO_x absorbent when the oxygen concentration around the NO_x absorbent lowers are capable of penetrating through and escaping from the outer oxide layer, the sulfur oxides are less accumulated in the under catalytic layer.

According to another aspect of the invention, the exhaust gas purifying catalyst comprises an under catalytic layer, disposed on a substrate, which has a NO_x reducing catalyst for deoxidizing and reducing NO_x in exhaust gas, a NO_x absorbent for absorbing NO_x in exhaust gas under existence of oxygen, releasing the absorbed NO_x when the oxygen concentration of exhaust gas lowers, and restrained from absorbing NO_x by sulfur compounds in exhaust gas, and a promotor or auxiliary catalyst for absorbing oxygen in exhaust gas and releasing the oxygen when the oxygen concentration in exhaust gas lowers, and an outer oxide layer, disposed over the under catalytic layer, which contains a Ce-Zr composite oxide higher in acidity than the auxiliary catalyst.

The acidity difference such that the auxiliary catalyst in the under catalytic layer is lower in acidity than the Ce-Zr composite oxide in the outer oxide layer provides a tendency to distribute sulfur more densely in the outer oxide layer than in the under catalytic layer, so as to more effectively prevent sulfur poisoning of the NO_x absorbent. While the NO_x absorbent somewhat lowers its NO_x absorbing performance if the auxiliary catalyst in the under catalytic layer attains acidity as high as the outer oxide layer, the auxiliary catalyst having low acidity acts profitably on the NO_x absorbing performance of the NO_x absorbent.

The auxiliary catalyst preferably comprises one of ceria, Ce-Zr composite oxides and composite oxides of Ce, Ti and other metals.

The exhaust gas purifying catalyst may further comprise an in-between layer disposed between the under catalytic layer and the outer oxide layer for activating NO_x. The in-between layer separates the under catalytic layer and the outer oxide layer from each other to prevent the outer oxide layer from blocking NO_x absorption by the NO_x absorbent in the under catalytic layer. Further, the in-between layer activates NO_x, so as to profitably act on the NO_x absorbing performance of the NO_x absorbent.

As the auxiliary catalyst, while it is advantageous to employ ceria in the viewpoint of oxygen absorption performance, nevertheless, a Ce-Zr composite oxide, which has high heat-resistance, is preferably employable in the light of that the exhaust gas purifying catalyst is

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exposed to exhaust gas at significantly high temperatures.

5 A noble metal may be contained as a catalytic metal in the NO_x reducing catalyst. As noble metals have catalytic activity to NO_x deoxidization and reduction from a relatively low temperature, the exhaust gas purifying catalyst profitably acts on NO_x purification.

10 The NO_x absorbent preferably comprises at least one selected from a group including alkaline earth metals, alkali metals and rare earth elements for the reason that these metals and elements have high basicity and are, in consequence, advantageous to NO_x absorption. Ba may be most preferably employable. Further, the NO_x absorbent may be preferable to be lower in 15 acidity than the Ce-Zr composite oxide because NO_x is apt to be adsorbed by high acid materials.

15 The exhaust gas purifying catalyst comprising an under catalytic layer containing a NO_x absorbent and an outer oxide layer containing a Ce-Zr composite oxide in accordance with a preferred embodiment prevents the NO_x absorbent in the under catalytic layer from sulfur poisoning without a significant loss of NO_x absorption performance.

20 The exhaust gas purifying catalyst comprising an under catalytic layer containing a NO_x reduction catalyst, a NO_x absorbent and an auxiliary oxygen absorption catalyst and an outer oxide layer containing a Ce-Zr composite oxide higher in acidity than the auxiliary oxygen absorption catalyst in accordance with a preferred embodiment causes the state in which the 25 sulfur concentration in exhaust gas easily becomes lower in the under catalytic layer than in the outer oxide layer, which is advantageous to prevention of sulfur poisoning of the NO_x adsorbent and improvement of NO_x absorption performance.

30 The incorporation of an in-between layer for activating NO_x prevents the oxide layer from blocking NO_x absorption of the NO_x absorbent and beneficially acts on NO_x absorption of the NO_x absorbent.

35 The foregoing and other objects and features of the present invention will be clearly understood from the following detailed description with respect to the preferred embodiment thereof when reading in conjunction with the accompanying drawings, in which:

40 Figure 1 is a schematic cross-sectional view of an exhaust gas purifying catalyst of the invention;

45 Figure 2 is a graphical diagram showing the relationship between Zr molar fraction of a Ce-Zr composite oxide and ionic electric field strength; and

50 Figure 3 is a graphical diagram showing NO_x conversion efficiency of an example exhaust gas purifying catalyst of the invention and a comparative exhaust gas purifying catalyst.

55 Referring to the drawings in detail and, in particular, to Figure 1, there is shown a layer structure of an exhaust gas purifying catalyst 100 for a vehicle of the type which alters an air-fuel mixture between a lean side on which an excess air ratio λ is greater than one (1) and a rich side on which the excess air ratio λ is equal to or smaller than one (1) in accordance with engine operating conditions. On the lean side, the air-to-fuel ratio is between 22 and 100 and the oxygen concentration of the exhaust gas is higher than 5 %. The exhaust gas purifying catalyst 100 comprises three catalytic layers, namely an under catalytic layer 2, an in-between

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catalytic layer 3 and an outer catalytic layer 4, i.e. an oxide layer, supported on a substrate 1. The substrate 1 is of a monolith type of cordierite honeycomb bed which has two cells per inch and six mil thickness wall between each adjacent cells. The under catalytic layer 2 contains a NOx absorbent and, more specifically, comprises Pt as a catalytic metal, Ba as a NOx absorbent, alumina as a carrier or support base material for carrying the Pt and Ba thereon, a Ce-Zr composite oxide as a promotor or auxiliary catalyst for absorbing oxygen and a hydration alumina binder. The in-between catalytic layer 3 comprises Pt and Rh as catalytic metals, zeolite as a carrier or support base material for carrying the Pt and Rh thereon and a hydration alumina binder. The outer catalytic layer 4 comprises a Ce-Zr composite oxide and a hydration alumina binder. Each of the in-between and outer catalytic layers contains Pt as a part of catalytic metal and Ba as a part of NOx absorbent. The Ce-Zr composite oxide is different in Zr concentration between the under catalytic layer 2 and the outer catalytic layer 4 and, more specifically, higher in the outer catalytic layer 4 than in the under catalytic layer 2. In consequence, the acidity of Ce-Zr composite oxide is higher in the outer catalytic layer 4 than in the under catalytic layer 2.

20 An example exhaust gas purifying catalyst was prepared in the following process.

A slurry was prepared by adding nitric acid to a mixture of alumina, a Ce-Zr composite oxide and hydrate alumina mixed at a weight ratio of 46.5 : 46.5 : 7. The nitric acid was added in order to adjust the potential of hydrogen (pH) of the mixture slurry between approximately 3.5 and 4. A honeycomb substrate 1 was dipped in the mixture slurry and then pulled out from the mixture slurry. After blowing off an excess of the mixture slurry from the honeycomb substrate 1 with air, the mixture slurry remaining applied on the honeycomb substrate 1 was dried at 150°C for two hours and sintered at 500°C for two hours so as thereby to be formed as an under catalytic layer 2. Through the process, the total weight of alumina, Ce-Zr composite oxide and binder was adjusted to 320 g/L which corresponded to 80 weight % of the honeycomb substrate 1. In the specification, the unit g/L is referred to the weight per one liter of the honeycomb substrate 1. As the Ce-Zr composite oxide, $Ce_{0.6}Zr_{0.4}O_2$ which had a Zr molar fraction i.e. $Zr/(Ce + Zr)$, of 0.4, was employed. The Ce-Zr composite oxide having a Zr molar fraction is hereafter referred to as an A-2 Ce-Zr composite oxide. A slurry was prepared by adding water and a zeolite (MFI) powder to a mixture of dinitro-diamine platinum solution and rhodium nitrate solution mixed so as to contain Pt and Rh at a weight ratio of 75 : 1. The total weight of Pt and Rh was adjusted to 24 g per 1 Kg zeolite. After drying the mixture slurry by a spray dryer, the mixture slurry was sintered at 500°C for two hours to provide a Pt-Rh carrying zeolite powder. A slurry was prepared by adding water to the Pt-Rh carrying zeolite powder and hydrate alumina at a weight ratio of 85 : 15. The honeycomb substrate 1 formed with the under catalytic layer 2 was dipped in this mixture slurry and then pulled out from the mixture slurry. After blowing off an excess of the mixture slurry from the honeycomb substrate 1 with air, the mixture slurry remaining applied on the honeycomb substrate 1 was dried at 150°C for two hours and sintered at 500°C for two hours so as thereby to be formed as an in-between catalytic layer 3 over the under catalytic layer 2. Through the process, the total weight of Pt and Rh carried on the zeolite was adjusted to 20 g/L which corresponded to 5 weight % of the honeycomb substrate 1. A slurry was prepared by adding water to a mixture of a Ce-Zr composite oxide and hydrate alumina at a weight ratio of 10 : 1. As the Ce-Zr composite oxide, $Ce_{0.4}Zr_{0.6}O_2$ whose Zr molar fraction was 0.6, was employed. The Ce-Zr composite oxide having a Zr molar fraction of 0.6 is referred to as an A-3 Ce-Zr composite oxide. The honeycomb substrate 1 formed with the under

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and in-between catalytic layers 2 and 3 was dipped in this mixture slurry and then pulled out from the mixture slurry. After blowing off an excess of the mixture slurry from the honeycomb substrate 1 with air, the mixture slurry remaining applied on the honeycomb substrate 1 was dried at 150°C for two hours and sintered at 500°C for two hours so as thereby to be formed as an outer catalytic layer 4 over the in-between catalytic layer 3. Through the process, the total weight of ceria was adjusted to 100 g/L which corresponded to 25 weight % of the honeycomb substrate 1. The honeycomb substrate 1, on which the multiple catalytic layer, i.e. the under, in-between and outer catalytic layers 2, 3 and 4, was formed, was dipped in a mixture of a dinitro-diamine platinum solution and a barium acetate solution so as to be impregnated with 6 g/L Pt and 30 g/L Ba and then dried at 150°C for two hours and sintered at 500°C for two hours.

In order to assess NOx conversion efficiency and anti-SOx poisoning property of the exhaust gas purifying catalyst as an example of the invention, a comparative sample exhaust gas purifying catalyst was prepared by simply replacing the A-3 Ce-Zr composite oxide with a Ce-Zr composite oxide having a Zr molar fraction of 0.2, i.e. $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$ (which is hereafter referred to an A-1 Ce-Zr composite oxide) or a Ce-Zr composite oxide having a Zr molar fraction of 0.9, i.e. $\text{Ce}_{0.1}\text{Zr}_{0.9}\text{O}_2$ (which is hereafter referred to an A-4 Ce-Zr composite oxide) in the exhaust gas purifying catalyst described above.

Impurities content of each of the example exhaust gas purifying catalyst according to the above embodiment and the comparative exhaust gas purifying catalyst was less than one weight %. The relationship between Zr molar fraction and ionic electric field strength for the A-1, A-2, A-3 and A-4 Ce-Zr composite oxides is shown in Figure 2.

Measurements of NOx conversion efficiency were performed by exposing the example exhaust gas purifying catalyst and the comparative exhaust gas purifying catalyst to simulated exhaust gas flowing at 150°C at a space velocity SV of 55000 h⁻¹ through a fluidized bed. Specifically, the simulated exhaust gas, which is specified in a table below, was altered in composition to a $\lambda = 1$ state (which refers to the state of exhaust gas discharged when an air-fuel mixture of an excess air ratio λ of 1 is burnt) from a lean state (which refers to the state of exhaust gas discharged when a lean air-fuel mixture is burnt) once, kept in the $\lambda = 1$ state for a specified period of time and thereafter returned to the lean state. The measurement was made to find NOx conversion efficiency for 130 seconds since the alteration to the lean state of the simulated exhaust gas. The result is shown as fresh NOx conversion efficiency in Figure 3.

Simulated Exhaust Gas Composition

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Component	$\lambda = 1$ State	Lean State
HC(Propylene)	4000 ppmC	4000 ppmC
CO	0.16 %	0.16 %
NOx	260 ppm	260 ppm
H ₂	650 ppm	650 ppm
CO ₂	9.75 %	9.75 %
O ₂	0.5 %	7 %
N ₂	Remainder	Remainder

5 Further in order to assess SO_x-poisoned NO_x conversion efficiency of the exhaust gas
purifying catalyst of the invention, after subjecting the example exhaust gas purifying catalyst
and the comparative exhaust gas purifying catalyst to SO_x-poisoning, measurements of NO_x
conversion efficiency were made by the same manner as described above. SO_x-poisoning was
10 performed by exposing each exhaust gas purifying catalyst to an N₂ gas containing 200 ppm of
SO₂ and 20 % of O₂ flowing at 350°C at a space velocity SV of 55000 h⁻¹ through a fluidized
15 bed for 30 minutes. The result is shown as SO_x-poisoned NO_x conversion efficiency in Figure 3.

15 As clearly seen in Figure 3, it is recognized that the Ba as the NO_x absorbent in the under
catalytic layer 2 has been poisoned by SO₂ from the fact that each exhaust gas purifying
20 catalysts shows a significant drop in SO_x-poisoned NO_x conversion efficiency. However, the
example exhaust gas purifying catalyst in which the A-3 Ce-Zr composite oxide or the A-4 Ce-Zr
25 composite oxide, which is higher in acidity than the A-2 Ce-Zr composite oxide, is contained in
the outer catalytic layer 4 shows a higher SO_x-poisoned NO_x conversion efficiency and provides a
lower drop ratio of NO_x conversion efficiency due to SO_x-poisoning than the comparative exhaust
30 gas purifying catalyst in which the A-1 Ce-Zr composite oxide having a low acidity is contained
in the outer catalytic layer 4. In consequence, it is concluded that the acidity of the Ce-Zr
35 composite oxide in the outer catalytic layer 4 affects NO_x conversion efficiency and the
increased acidity of the Ce-Zr composite oxide in the outer catalytic layer 4 works effectively
40 with respect to anti-SO_x poisoning property of the exhaust gas purifying catalyst. It is
considered to be one of the causes that SO₂ in the exhaust gas is easy to be absorbed by the A-
45 1 Ce-Zr composite oxide which is low in acidity and, however, is hardly absorbed by the A-3 Ce-
Zr composite oxide or the A-4 Ce-Zr composite oxide, which is high in acidity. That is, the
50 mechanism is considered to take the process of causing only a small amount of SO₂ to diffuse
in the under catalytic layer 2 due to disturbance by the outer catalytic layer 4, so as to
prevent Ba in the under catalytic layer 2 from SO_x-poisoning; causing NO_x to pass through the
outer catalytic layer, i.e. the oxide layer 4 without disturbance by the outer catalytic layer 4, so
as to be absorbed by Ba in the under catalytic layer 2; and permitting SO₂ to break away from Ba
and escape through the outer catalytic layer 4, so as to prevent SO₂ from accumulating in the
under catalytic layer 2. As a result of practical investigation of the sulfur concentration
distribution in the SO_x-poisoned exhaust gas purifying catalyst for which the utilization was
made of X-ray images, it was found that while the SO_x-poisoned example exhaust gas purifying
catalyst showed a lower sulfur concentration in the under catalytic layer 2 than in the outer
catalytic layer 4, on the contrary, the SO_x-poisoned comparative exhaust gas purifying catalyst
showed a higher sulfur concentration in the under catalytic layer 2 than in the outer catalytic
layer 4. Further, it was found that the Ce-Zr composite oxide was desirable to have a molar
fraction between 0.6 and 1.0 and, in particular, between 0.9 and 1.0 in view of refreshing and
anti-SO_x poisoning.

55 In the light of the above discussion, it is grasped that making the outer catalytic layer 4
be a layer of the A-3 Ce-Zr composite oxide which is higher in acidity than the A-2 Ce-Zr
composite oxide used as a promotor or auxiliary catalyst for oxygen adsorption in the under
catalytic layer 2 is effective in improving an anti-SO_x poisoning property. NO_x that is absorbed
by Ba in the under catalytic layer 2 while an air-fuel mixture remains lean ($\lambda > 1$) is released

when the air-fuel mixture is turned rich ($\lambda \leq 1$). The NOx that is released is deoxidized and reduced by Pt and Rh carried on zeolite in the in-between catalytic layer 3 as well as by Pt carried on alumina in the under catalytic layer 2. The in-between catalytic layer 3 works to activate NOx and promote adsorption of NOx by Ba in the under catalytic layer 2.

Although the present invention has been fully described by way of the preferred embodiments thereof with reference to the accompanying drawings, it is to be noted that various changes and modifications are apparent to those skilled in the art. Therefore, unless otherwise such changes and modifications depart from the true scope of the present invention, they should be construed as included therein.

15 **Claims**

1. An exhaust gas purifying catalyst comprising:

20 a substrate;

25 a catalytic layer containing a NOx absorbent which absorbs NOx in exhaust gas under existence of oxygen, releases said NOx when an oxygen concentration of said exhaust gas lowers and is restrained from absorbing NOx by sulfur compounds in said exhaust gas; and

30 an oxide layer containing a Ce-Zr composite oxide.

wherein said catalytic layer is disposed as an under layer on said substrate and said oxide layer is disposed as an outer layer over said oxide layer.

2. An exhaust gas purifying catalyst as defined in claim 1, and further characterized by:

35 a NOx reducing catalyst for deoxidization and reducing NOx in exhaust gas and an auxiliary catalyst for promoting oxygen adsorption which absorbs oxygen in said exhaust gas and releases said oxygen when said oxygen concentration lowers, wherein a catalytic layer containing said NOx reducing catalyst, said NOx absorbent and said auxiliary catalyst is disposed on a substrate and an oxide layer containing a Ce-Zr composite oxide which is higher in acidity than said auxiliary catalyst is disposed over said catalytic layer.

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3. An exhaust gas purifying catalyst as defined in claim 1 or 2, and further characterized by an in-between layer disposed between said catalytic layer and said oxide layer for activating NOx.

4. An exhaust gas purifying catalyst as defined in one or more of claims 1 to 3, wherein said NOx absorbent is lower in acidity than said Ce-Zr composite oxide.

55 5. An exhaust gas purifying catalyst as defined in one or more of claims 1 to 4, wherein said NOx reducing catalyst contains a noble metal as a catalytic metal.

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6. An exhaust gas purifying catalyst as defined in one or more of claims 1 to 5, wherein said NOx absorbent comprises at least one selected from a group including alkaline earth metals,
5 alkali metals and rare earth elements.

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FIG. 1

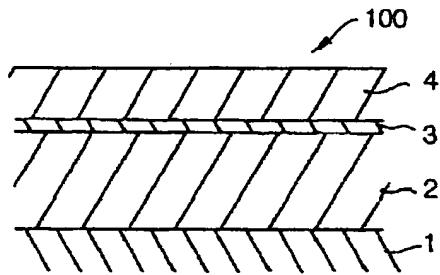
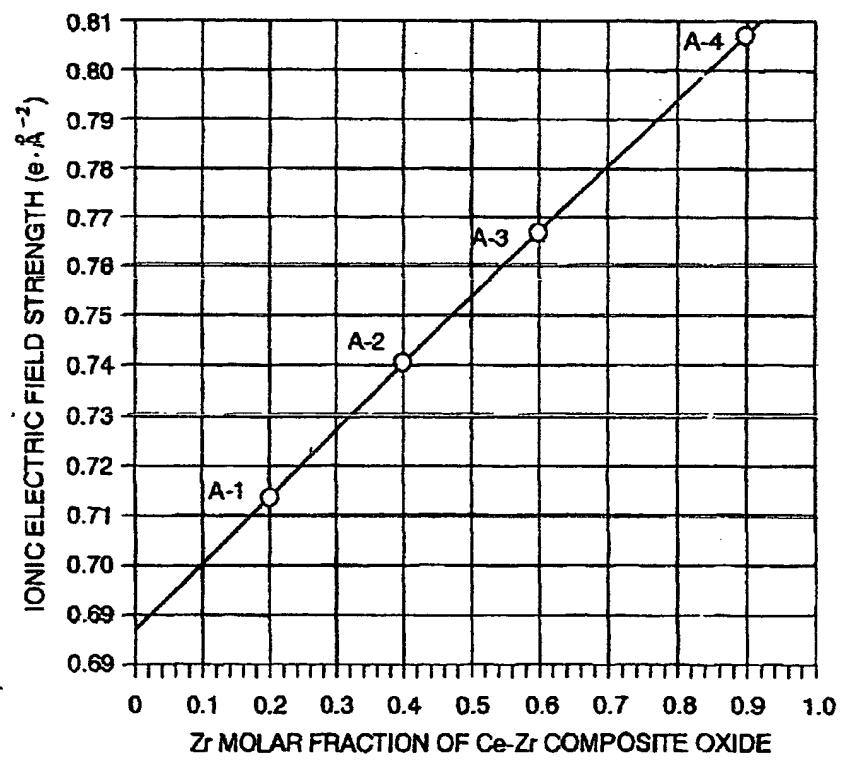
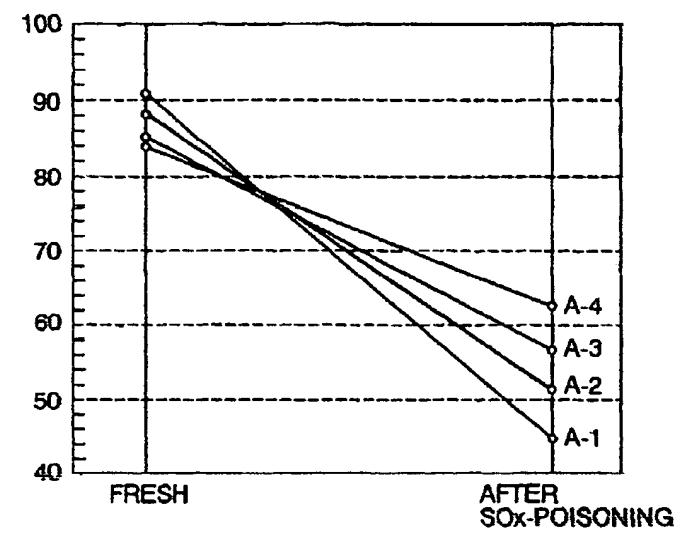


FIG. 2



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FIG. 3



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ANNEX TO THE EUROPEAN SEARCH REPORT
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This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
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